

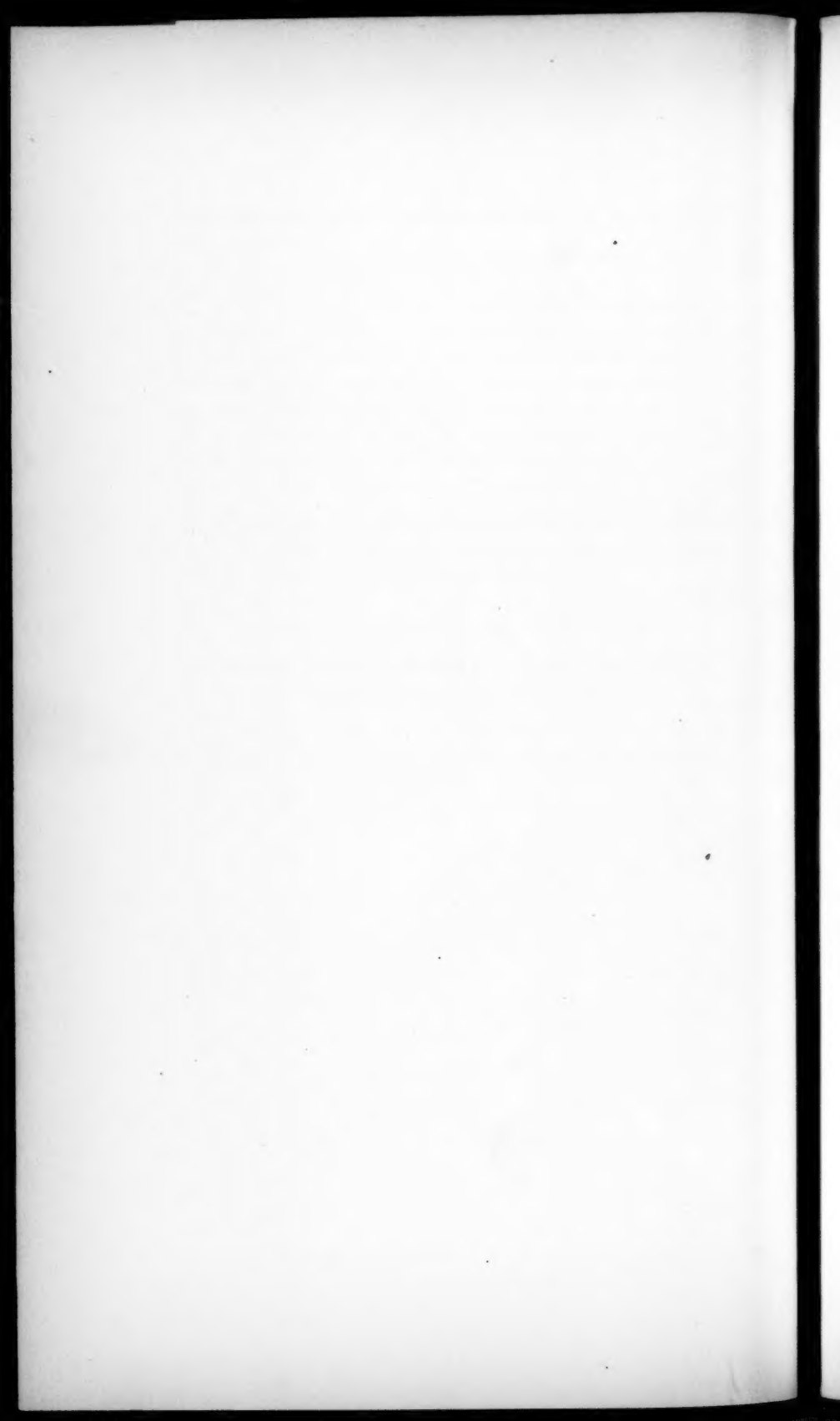
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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

*ON THE ACTION OF AMMONIA UPON CUPRI-
AMMONIUM ACETOBROMIDE.*

BY THEODORE WILLIAM RICHARDS AND ROBERT JAY FORSYTHE.



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It is well known that there is a large class of cupriammonium compounds which contain two molecules of ammonia for each molecule of the cupric salt. The compounds of this class are by far the most stable of the cupriammonium compounds; they are usually permanent in the air, and many of them may be heated above 100° without decomposition. They have, as a general rule, the power of absorbing more ammonia if exposed to an atmosphere of this gas; but the additional ammonia is expelled with the greatest ease. For this reason the compounds containing little ammonia have been assumed in the series of papers of which this is one to be the normal cupriammonium compounds, and any extra ammonia in any other class of compounds has always been designated in the name of this new class. For instance, "tetrammon-cupriammonium bromide" indicates $\text{Cu}(\text{NH}_3)_2\text{Br} \cdot 4 \text{NH}_3$ or $\text{CuBr}_2 \cdot 6 \text{NH}_3$.

To the class of stable normal cupriammonium compounds belongs the salt $\text{Cu}(\text{NH}_3)_2\text{BrC}_2\text{H}_3\text{O}_2$, which was recently discovered by one of us.* The possible absorption of more ammonia by this double salt promised to be a question of much interest; and it is with this question that the present paper is concerned.

A weighed amount of finely powdered pure cupriammonium acetobromide was introduced into a weighed glass tube, so drawn out and bent that the part containing the salt could be immersed in a freezing mixture. Through this tube was passed dry ammonia until the substance, which absorbed a large quantity of gas, remained constant in weight. In two experiments the weights were as follows:—

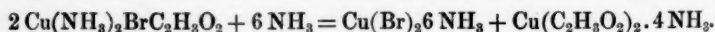
| | (1) | (2) |
|-------------------------------|-----------------|---------------|
| (2) Weight of substance taken | = 0.9904 | 1.4801 |
| Weight of substance found | = <u>1.2157</u> | <u>1.8090</u> |
| Gain in weight | 0.2253 | 0.3289 |

* Berichte der deutsch. ch. G., XXV. 1492.

The weights gained were equal to 22.7 per cent and 22.2 per cent of the original weight, while a gain of 3 NH₃ would have corresponded to 21.51 per cent. The error of this result is not greater than might have been expected, considering the fact that the deep blue powder was extremely hygroscopic, and that it was necessary to weigh the tube while this was still ice-cold, in order to avoid loss of ammonia. A single analysis, although not exact, served to confirm sufficiently the formula of the resulting substance.

(3) 1.809 grams of the substance required 29.6 cubic centimeters of normal acid to neutralize the ammonia contained in it. This corresponds to 28.2 of ammonia instead of the theoretical 30.3. The loss occurred during the transference from the tube to the retort, for the substance is excessively unstable.

The new substance, empirically CuBrC₂H₃O₂5NH₃, dissolved easily in water with the formation of a fine deep blue solution, which lost ammonia upon exposure to the air, and soon deposited a basic salt of copper. Exposed in a dry state to dry air, the substance lost ammonia with great rapidity, and turned distinctly green in color. The only green compound which could be formed under these conditions was Cu(NH₃)₂Br₂, and hence the color change was proof that the ammonia had decomposed the original cupriammonium acetobromide according to this reaction:—



Upon exposure to the air the compound CuBr₂6NH₃, which has recently been discovered in this laboratory,* is known to lose ammonia with conversion into the likewise newly discovered CuBr₂ · 2 NH₃.

The other compound represented above, Cu(C₂H₃O₂)₂4 NH₃, has not heretofore been made. Foerster, who tried to prepare it, was unable to make cupric acetate absorb anything like its full complement of ammonia, because he did not cool the mixture.† The only step necessary for the final proof of the reaction given above was then the preparation of diammon cupriammonium acetate, Cu(NH₃)₂C₂H₃O₂ · 2 NH₃, by the action of ammonia gas upon cupriammonium acetate at very low temperatures.

Under conditions precisely like those of Experiments 1 and 2, the two following syntheses were made:—

| | (4) | (5) |
|--|----------|--------|
| Weight of Cu(NH ₃) ₂ (C ₂ H ₃ O ₂) ₂ taken | = 0.4380 | 1.0324 |
| Weight of substance formed | = 0.5160 | 1.2082 |
| Gain in weight | 0.0780 | 0.1758 |

* Berichte der deutsch. ch. G., XXIII. 3790.

† Ibid., XXV. 3416.

The gains were then 17.8 per cent and 17.0 per cent of the weight of substance taken, while the formula $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_3$ requires a gain of 15.8 per cent. Here again the error is due to the great hygroscopic power of the resulting compound, — which absorbed all of the traces of water in the ammonia, — as well as to the fact that the tube had to be weighed while very cold. Since the errors in an analysis of the final compound must necessarily, as before, be in the opposite direction to the errors just cited, the following analysis was made: (6) 1.208 grams of substance required for neutralization 18.75 cubic centimeters of normal acid, thus having contained 26.5 per cent of ammonia. The theoretical amount corresponding to $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{NH}_3$ is 28.0 per cent. Greater exactness than this would have demanded great elaboration of experimental detail, on account of the excessive instability of the compound.

These analyses and syntheses afford conclusive evidence that the compound diammon cupriammonium acetate exists, and that it, together with the most highly ammoniated cupriammonium bromide, is formed by the action of ammonia upon cupriammonium acetobromide.